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by

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CHEMISTRY WITHIN VAN DER WAALS CLUSTERS OF UNSATURATED MOLECULES: OBSERVATION OF CATIONIC POLYMERIZATION

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ABSTRACT. We present in this paper the observation of intracluster ion-molecule polymerization reactions within clusters containing molecules which possess double or triple carbon-carbon bonds. This effect is borne out by the observation of unusual magic numbers in the cluster ion distribution only under expansion conditions which favor the production of large neutral clusters. These magic numbers are rationalized in term of the production of covalently bonded cyclic molecular ions which terminate the cationic polymerization process.

1. Introduction

A subject of great interest in recent years has been the study of the physics of weakly bound van der Waals clusters. These species have been probed in a variety of ways to gain an understanding of their formation and to determine their various physical properties. However, the study of chemical reactions within clusters is especially intriguing since clusters can conceptionally bridge the disparate fields of bimolecular gas-phase reaction dynamics and solution chemistry. The ultimate goal of these studies is to obtain an understanding of the factors that govern reactions in solution but which are absent in gas phase processes. By concentrating on the chemistry within these cluster systems one can directly observe how the behavior of the system changes as a function of stepwise solvation.

Most of the recent work in this area consists of utilizing the neutral cluster as one of the reagents for a bimolecular reaction[1-8] with the product cluster ion being directly detected via conventional mass spectrometric techniques. Apart from the observation of protonated clusters {i.e., $(H_2O)_nH^+$,[9] $(NH_3)_nH^+$,[10,11] $(CH_3COCH_3)_nH^+$,[12] $(CH_3OH)_nH^+$,[13] $(CH_3OCH_3)_nH^+$,[13] and a few heterocluster ions such as $[(ROH)_n(H_2O)_m]H^+$[14,15] and $[(CH_3OH)_n(H_2O)_m]H^+$,[16] } there are few reported cases of chemical reactions taking place within the cluster ion itself.[12,16-20] Yet it has been known that electron impact ionization of clusters leads to ions that closely resemble many of the intermediates found in bimolecular ion-molecule reactions.[21,22]

In addition to this typical unimolecular and bimolecular gas-phase chemistry already stud-

ied within clusters, our group has recently observed the generation of new cluster product ions which cannot be explained by either of these two known processes. That is, we observe product ion formation that has absolutely no counterpart with gas-phase bimolecular reactions and which only occurs within a van der Waals cluster[23]. These new processes, which we have begun to document in the past four years at SUNY, include the generation of $(C_2H_4F_2)_{n\geq4}H^+$ ions from 1,1-difluoroethane clusters[24], the generation of $(CH_3OCH_3)_nH_3O^+$ & $(CH_3OCH_3)_nCH_3OH_2^+$ ions from dimethyl ether clusters[25,26], the generation of $(NH_3)_nN_2H_5^+$ ions from ammonia clusters[27] and the photogeneration of MoO^+ and MoO_2^+ ions from van der Waals clusters of molybdenum hexacarbonyls[28]. The observation of these new chemical processes which occur only within a cluster, is particularly exciting for chemists in that we may now utilize clusters as a novel "crock-pot" in which to produce new molecules, which could not be produced be any other means.

The majority of our experiments consist of generating a beam of neutral van der Waals clusters and then, by electron impact, performing mass spectroscopy on the ion cluster species generated within the molecular beam. Though the cation within the cluster is rapidly generated ($\sim10^{-14}$ s), it takes microseconds before the generated cluster ion is mass selected by the quadrupole filter. On such a lengthy time scale the cation within the cluster may rid itself of its excess energy either by fragmentation, evaporation of neutral monomers or the solvated cation may chemically react with one (or more!) of the solvating neutrals. In any case, a new product cluster ion has been generated, which is then detected via mass spectroscopy.

One may therefore visualize the electron impact ionizer of our mass spectrometer as a 'reaction cell' in which the precursor cluster ion is generated and allowed to 'incubate' for microseconds. After this time period the newly generated product cluster ions are subsequently analyzed via mass spectroscopy. By observing the distribution of product cluster ions in the mass spectra, we can then deduce the ion-molecule chemistry which is occurring within the bulk cluster, and monitor how this chemistry changes as a function of cluster size.

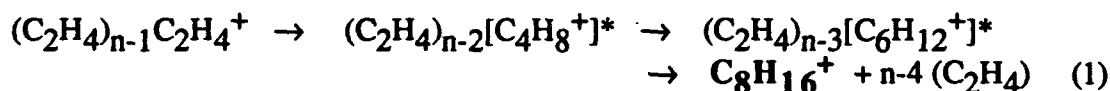## 2. Results and Discussion

2.1 ETHYLENE CLUSTERS[29]

The ethylene cluster mass spectrum is quite simple in that it is composed of a single sequence of cluster ions with the formula $(C_2H_4)_n^+$, which one would naturally attribute to the unreacted parent cluster ion.We observe that at decreased nozzle temperature (or increased stagnation pressure, 1.5-3.5 atm)[30] a pronounced ion intensity (i.e., magic number) appears for the empirical formula $(C_2H_4)_4^+$, such that it dominates the entire spectrum.

This observation of n=4 being a magic number only under certain expansion conditions is difficult to explain solely in terms of stabilities of either the neutral or ionic parent ethene clusters. A closed solvent shell, hydrogen bonded to a central cation, is typically the driving force for the appearance of a magic number in a molecular cluster. In a system, such

as ethene, where hydrogen bonding does not play a significant role, the observation of pronounced magic numbers is therefore not expected since the distribution of neutral clusters is produced by processes which are essentially statistical in nature (i.e., why should the $(C_2H_4)_4^+$ cluster ion be so stable?). There would seem to be no *a priori* reason to predict that any particular ethene cluster size should be extraordinarily stable. High pressure mass spectrometry[30] has shown that the $C_2H_4^+$ cation undergoes an exothermic condensation reaction with a neutral C_2H_4 molecule to form a branched $C_4H_8^+$ cation. This new $C_4H_8^+$ cation can then undergo successive reactions with additional C_2H_4 molecules to form a larger and larger branched cation with the general formula $C_{2m}H_{4m}^+$. The rate of each successive condensation reaction decreases rapidly as the extent of the branching of the product cation increases, This drop in the reaction rate has been attributed to steric effects (i.e., highly branched $C_{2m}H_{4m}^+$ product cations being less reactive)[30].

We now speculate that the ethene cluster ions we observe represent the products of a similar series of intracluster condensation reactions. That is, the observation of the magic number at n = 4 (under expansion conditions which create extensive clustering) is due to the formation of the $C_8H_{16}^+$ molecular ion generated via a series of successive ion-molecule reactions within the cluster. Since these condensation reactions are exothermic[31] we would then also expect extensive evaporation of unreacted monomers (as seen before with the ammonia system).

In summary, neutral $(C_2H_4)_n$ clusters with n > 4, following ionization via electron impact, can react within the cluster to give primarily the $C_8H_{16}^+$ cation as shown in reaction (4). The intensity of these ions would then be

$$(C_2H_4)_{n-1}C_2H_4^+ \rightarrow (C_2H_4)_{n-2}[C_4H_8^+]^* \rightarrow (C_2H_4)_{n-3}[C_6H_{12}^+]^*$$
$$\rightarrow C_8H_{16}^+ + n\text{-}4\,(C_2H_4) \quad (1)$$

expected to increase as the distribution of the neutral ethene clusters grows larger (i.e., as either $T_0 \downarrow$ or $P_0 \uparrow$: n $\uparrow$). The prominent peak at n = 4 represents a balance between two competing effects: the larger the cluster the greater the probability of reaction 1, however, as the cluster size increases the rate constants of each individual step decrease. This is a new interpretation in that this particular magic number is attributed not to a central cation solvated by neutral monomers but rather due to the generation of a new molecular ion. We have recently additional studies of clusters containing ethene, 1,1-difluoroethene and propene and have again observed similar phenomena: observation of magic numbers which are consistent with the generation of cyclic molecular ions[32]. These results indicate that cluster cationic polymerization is indeed a common reaction for the family of olefinic van der Waals clusters.

2.2 ACETYLENE/ACETONE CLUSTERS[33]

Under the expansion conditions utilized, three classes of 'cluster' ions may be observed in

the acetylene/acetone cluster mass spectra: 1) neat acetylene ions, 2) neat acetone ions, and 3) heterocluster ions (i.e., $A_nT_m^+$ where $A = C_2H_2$ and $T = CH_3COCH_3$). The behavior of the first two classes of ions is consistent with previous reports[12,15] and will only be briefly considered here. At the highest stagnation pressure utilized in the present experiments (2.0 atm.), it was not possible to observe neat acetylene cluster ions higher than the trimer which may be attributed to the production of benzene cations[34,35] within the acetylene clusters followed by evaporative losses of the remaining monomers as shown in reaction (2).

$$A_n^+ \rightarrow C_6H_6^+ + (n\text{-}3)\,A \qquad (2)$$

Two main series of heterocluster ion were observed, A_nT^+ and $A_nC_2H_3O^+$. All of the $A_nT_m^+$ clusters displayed very similar behavior with the $A_2T_m^+$ ions always becoming very prominent as the expansion pressure was increased for m = 1-4. We also note that the $A_2C_2H_3O^+$ ions are the most intense ions under all of the expansion conditions investigated with very little intensity observed beyond n = 3.

We feel, in light of our previous work, that the A_2T^+ and $A_2C_2H_3O^+$ ions represent the covalently bonded molecular ions $C_7H_{10}O^+$ and $C_6H_7O^+$, respectively via intracluster ion-molecule association reactions. The pressure behavior exhibited by the data is very reminiscent of that obtained for neat olefin clusters as indicated in section 2.1. We propose that ionization of acetylene/acetone clusters leads to the production of $C_7H_{10}O^+$ and $C_6H_7O^+$ ions The fact that the magic number occurs for n = 2 is also suggestive of the formation of a molecular ion in this system since this corresponds to replacement of one acetylene by an acetone (or acetyl) during the ionic reaction (i.e., 2 C_2H_2 + $CH_3COCH_3^+$ or $2C_2H_2$ + CH_3CO^+).

Unfortunately the present mass spectral data do not allow us to unequivocally assign the structures of the $C_7H_{10}O^+$ and $C_6H_7O^+$ ions but previous investigations of the ion-molecule chemistry of acetone[36] as well as the polymer chemistry of carbonyl compounds[37], suggest that a reaction across the C=O bond should give rise to an ether linkage (i.e., a C-O-C bond). If the reaction proceeds by initial production of an acetone ion within the cluster, the product ion is formed via reaction (3).

$$A_nT_m + e^- \rightarrow A_nT_{m\text{-}1}CH_3COCH_3^+ + 2\,e^- \rightarrow C_7H_{10}O^+ + (n\text{-}2)\,A + (m\text{-}2)\,T \quad (3)$$
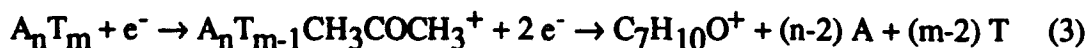
If this reaction is halted by production of a six-membered ring, as appears to be the case for neat acetylene clusters, the 2,2-dimethyl-2H-pyran radical ion would appear to be the expected product.

If the reaction proceeds by initial production of an acetyl ion (CH_3CO^+) within the cluster, the reaction will proceed as shown in reaction (4)

$$A_nT_m + e^- \rightarrow A_nT_{m\text{-}1}CH_3CO^+ + CH_3 + 2\,e^- \rightarrow C_6H_7O^+ + (n\text{-}2)\,A + (m\text{-}2)\,T \quad (4)$$
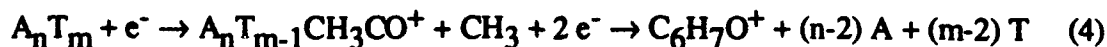
If the reaction is halted by production of a six-membered ring, then the expected ion product will be the 2-methylpyrylium ion ($C_6H_7O^+$). The fact that the $A_nC_2H_3O^+$ ion intensity distribution shows anomalous features under all expansion conditions, and very little intensity beyond n = 3, may indicate that reaction sequence (4) is not responsible for the exclusive production of the $C_6H_7O^+$ ions and may also arise from fragmentation of excited ions.

The present results suggest that it is possible to synthesize relatively complex molecules starting from simple molecular 'building blocks' within van der Waals clusters through ion-molecule reactions. Because of the differing stabilities and reactivities of ionic and neutral molecules, this method may be useful in production of ions of unusual structure, as well as providing insight into the basic mechanisms of ionic polymerizations and is a source of continuing study within our group.

3. Future Directions

The examples just shown represent the beginning of a new distinctive chemistry which can occur within the environs of a gas phase cluster. New experimental techniques which our group hopes to employ within the near future include the use of mass selected cluster beams to directly observe reaction dynamics, and the application of spectroscopic probes, such as laser induced fluorescence, to probe the internal states of the radical product generated via these cluster reaction.

Acknowledgements

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